

Permeselectives Properties Measurements of Low Density Polyethylene

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Abstract: On a fundamental level, the transition temperature (T_g) marks the transition from a cooperative mobility (T > T_g, rubbery state) to a localized mobility (T < T_g, glassy state). Fickian diffusion in polymers is an idealized case of mass transport, corresponding to a free diffusion of permeant without interactions with the molecular conformation of the polymer and then with its structural relaxation. There is a direct relationship between the diffusion and relaxation of the polymer and on whether we place ourselves below (glassy state) or above (rubbery state) of the glass transition temperature T_g, the diffusion mechanisms are very different. There are two types of models to describe the variation of the diffusion coefficient D. In this contribution, we will review the different behaviors of the distribution function of the T_g and show us the Deborah number D - α defined as the ratio of characteristic times of diffusion and relaxation, to indicate the nature of dissemination and to apply the model. As a practical example we have studied the case of low density polyethylene manufactured and processed by the national Algerian plastic society ENPC.

Key words: Diffusion • Permeation • Polyethylene

INTRODUCTION

The permeation of a permeant through a polymer occurs following 3 steps: the sorption of permeant, its diffusion through the polymeric film and desorption on the other side of the film.

The diffusion theory is based on the assumption that the flux of material diffusing per unit area and time through a substance is proportional to the concentration gradient.

In the case of a steady state, this relationship led to the first Fick's law:

$$j = -D \frac{\partial C}{\partial x} \quad (1)$$

The case of unsteady flow (where the concentration gradient depends on the time) is described by Fick's second law:

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \quad (2)$$

The solution of the Fick equation has been the subject of many studies and in many cases the object of interest is the mass fraction M_t of absorbed substance inside the polymer:

$$M_t = \int_{-\infty}^{+\infty} C \cdot dx \quad (3)$$

C is the concentration in an elementary layer dx at an abscissa x.

The kinetics of sorption of a polymer can be expressed by:

$$\frac{M_t}{M_\infty} = k \cdot t^n \quad (4)$$

M_t: mass fraction of absorbed substance

M_∞ : Quantity of absorbed substance at equilibrium

k : Constant

n : Parameter that varies depending on the mode of sorption

n = ½ defined type I sorption that occurs when the system polymer / permeant obeys to a Fickian diffusion. The sorption rate does not depend on the speed of swelling of the polymer [1].

Type II sorption corresponds to n = 1. This mode of sorption occurs when the rate of diffusion of permeant molecules is greater than the rate of relaxation of polymer chains. This kind of behavior (non Fickian) corresponds

to the behavior of organic vapors in glassy polymers. The kinetics of sorption is highly dependent on the rate of swelling of the polymer [2].

The case when n is between $\frac{1}{2} < n < 1$ is called the non-Fickian sorption. It occurs when the rate of diffusion of permeant molecules is of the same order as the relaxation rate of the polymer. However, no current theory is able to adequately explain this behavior [3].

When the permeant molecules do not interact with the polymer (the case of simple gases) the diffusion coefficient D is constant. But otherwise, the diffusion coefficient D is dependent on several factors.

The first distribution will depend on the nature of the polymer, the mobility of its chains, the degree of cross linking, the degree of crystallinity, etc. The glass transition temperature is a parameter that describes fairly thoroughly the nature of the polymer, because it marks the transition from a localized mobility ($T < T_g$, glassy state) to a cooperative mobility ($T > T_g$, rubbery state).

Using Deborah number (α_D) to describe diffusion in polymers was proposed by Vrentas *et al.* [4] and [5], in fact it is the ratio between the duration of the experiment reported in the lifetime of the observed phenomenon. The glass transition is defined by a number of Deborah equal to 1.

For different polymers, it was found that the diffusion coefficient increases with decreasing the glass transition temperature. This is illustrated by the (Fig. 1) obtained by Brown *et al.* [6].

Solving Fick's differential equation for the steady state allows access to the coefficient D_L (cm^2 / s) from the equation:

$$D_L = \frac{L^2}{6t_L} \quad (5)$$

Where L is the film thickness in cm and t_L the time lag in seconds.

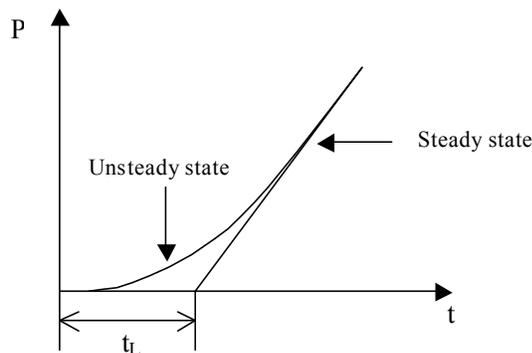


Fig. 1: Measurement of the diffusion coefficient D by the time lag method

A second method for determining the diffusion coefficient can be used. It is based on the inflection point I of the permeation curves corresponding to a time $t_{0.24}$ and a value of $J/J_{st} = 0.24$:

$$D_t = \frac{0.091.L^2}{t_{0.24}} \quad (6)$$

Permeation is the penetration of the permeate through the polymer and is related to a material's intrinsic permeability.

The process used leads directly to an accumulated quantity of permeant Q (time-lag method) or the transfer rate dQ/dt (differential permeation). The study of establishment and access to the steady flow can directly obtain the diffusion coefficients D and permeation P . The solubility coefficient σ can then be deduced.

MATERIALS AND METHODS

To carry out our measurements, we have been led to use the permeation and diffusion device developed in the BPM laboratory (UMR 6522, CNRS), University of Rouen (France). This instrument is extensively described in the work of S. Marais *et al.* [7, 8, 9].

Low-density polyethylene films were obtained by extrusion of granules supplied by Skikda-ENIP Company (reference B24/2, east Algeria). The density (d) and melt index (M_i) given by the supplier are respectively $d = 0.923$ and $M_i = 0.3$ g/min. This extrusion performed at ENPC-Chlef Company (west Algeria) leads to the formation of films.

The measurement method assumes that the flux J (L, t) through the dry surface can be expressed by:

$$J(L, t) = \frac{f}{A} \cdot 10^6 \cdot \frac{x^{out} - x^{in}}{RT_r} \cdot p_t \quad (7)$$

- A : Area of exposed film (30 cm^2)
- R : Perfect gas constant ($0.082\text{-atm}\cdot\text{cm}^3\cdot\text{K}^{-1}\cdot\text{mmol}^{-1}$)
- T_r : Temperature of experiments in K.
- f : Dry gas flow $\text{cm}^3\cdot\text{s}^{-1}$.
- x_{in} and x_{out} : Concentrations at the inlet and outlet gas sweep ppmV.
- p_t : Total pressure (1 atm).
- $J(L, t)$: Flux $\text{mmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$.

x_{in} concentrations and x_{out} are obtained directly to oxygen and indirectly to water from the dew point of the sweep gas.

From the steady state it is then possible to determine the permeability P of the film:

$$P = \frac{J_{st}L}{\Delta a} \quad (8)$$

With J_{st} : Steady flow

Δa : Difference in activity between the two sides of the film

The expression of the normalized flux variation (JL) according to the reduced quantity t/L^2 allows to standardize the quantities involved on the one hand and to ignore the sample thickness L on the other.

For water permeation study, the sample is first stored in a vacuum dryer for at least 12 hours at room temperature. It is then inserted into the measuring cell. A purge is then performed to dry up the film and the cell by the scans of ultra pure nitrogen (Cell downstream: receptor compartment) and pure (Upstream cell: donor compartment). The average thickness is obtained from 21 measurements with a micrometer (ROCH 0-25) in different parts of the sample surface.

The flow of purge gas is fixed at 3.3 cm³/s during the first ten hours of drying, then to 9.3 cm³/s until the signal stabilizes (dew point below -68°C).

After closing the nitrogen supply, the donor compartment is then quickly fed with pure liquid water. The filling time is very short, about 30 seconds and can be neglected at the time required to obtain the steady state.

The experiment consists in the acquisition and recording, with time, the following measures:

- Dew point temperature Tr (Shaw)
- Dew point temperature Tr (mirror)
- Cell temperature
- Relative Humidity

Experimentally, increasing the dew point temperature TR of dry gas, corresponding to its enrichment moisture is recorded as a function of time until the steady state.

The frequency in data acquisition is 1 point every 10 seconds.

After grading, shaping and fitting the two initial curves, obtained from the two probes, we obtain a single curve that will benefit from the qualities of each hygrometer: the speed of the capacitive probe (transient state) and precision of the probe mirror (initial state and steady state).

The experimental curves, as shown in the figure (Fig. 2) show three characteristic zones:

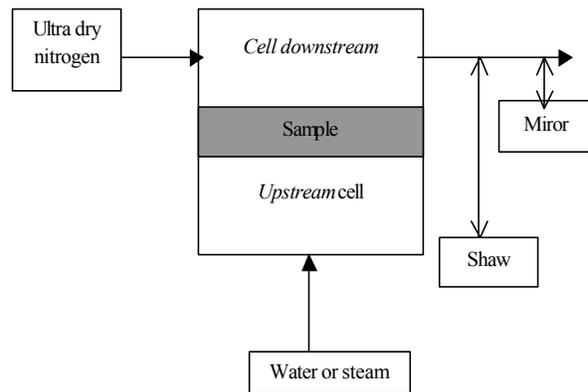


Fig. 2: Schematic of operating principle of the permeameter

- A significant flow for an hour or more (priming regime).
- An increasing flow for several hours (setting regime).
- A constant flow (steady state).

The priming time and duration of scheme property are directly related to the diffusivity of water in the polymer.

RESULTS AND DISCUSSION

The experimental results obtained on the permeameter for different polymers are presented on the (Table 1).

The permeability values ranged from 0.42 10⁻⁹ mmol.cm⁻¹.s⁻¹ (Polyimide) and 37.6 10⁻⁹ mmol.cm⁻¹.s⁻¹ (Polyethersulfone) or 40 to 4000 Barrer.

The diffusion coefficient D_L varies from 0.1 10⁻⁸ cm⁻².s⁻¹ (Polyimide) to 7.42 10⁻⁷ cm⁻².s⁻¹ (Polyethylene). LDPE, semi-crystalline polymer, with a particular molecular structure is characterized by the lowest quantity of sorbed water. This result is certainly due to the highly hydrophobic nature of low density polyethylene.

The permeation coefficients are measured when the regime is fully established; the variations of this property are less pronounced than those of diffusion. However, the neutral LDPE (P = 32 Barrer) appears to be less permeable than stabilized LDPE (P = 43 Barrer), these results are presented in the table (Table 2).

A comparison with bibliographic data allows us to situate our results, for comparable experimental conditions. Table (Table 2) allow verifying the consistency of the magnitude of values.

Literature data given in (Table 2) showed that apart from the value of 0.31 g.mm.m⁻².d⁻¹ for sample (a), the permeation coefficients are between 0.11 g. mm.m⁻².d⁻¹ (b) and 0.14 g.mm.m⁻².d⁻¹ (c) for most of polyethylene samples studied. Polyethylene manufactured in Algeria

Table 1: Experimental values of permeability and diffusion coefficients for different polymers

	LDPE	Polyetherimide	Polyetheretherketone	Polyimide	PET	PES
Thickness L 10 ⁴ cm	250	250	250	250	164	250
P.10 ⁹ mmol.cm ¹ .s ⁻¹	0.77	3.44	4.07	0.42	4.76	37.6
P Barrer	73	324	384	40	450	3550
D _t .10 ⁷ cm ² .s ⁻¹	7.42	0.66	0.73	0.10	0.56	2.06

Table 2: Comparison of experimental values of LDPE permeability coefficients with those of the literature

	(a)	(b)	(c)	(d)	Neutral LDPE (e)	Stabilized LDPE (f)
P.10 ⁹ g.mm.m ⁻² .j ⁻¹	0.31	0.11	0.14	0.12	0.06	0.07
Temperature °C	38	25	21	25	25	25

(a) Permeability and other film properties of plast. and elasto. Plastic Design Library, Norwich & NY, (1995)

(b) J. Crank and G.S. Park, Diffusion in polymers, Academic Press, London & NY, (1968)

(c) L. Hes, A. C. Bernado and M.A. Queiros, Polymer Testing, 15 (1996) 189-201

(d) S.Marais, Thèse de doctorat, Université de Rouen (1998)

(e) and (f) present relatively lower permeation coefficients in regard with literature data, namely 0.06 g.mm.m⁻².d⁻¹ for neutral LDPE and 0.07 g.mm.m⁻².d⁻¹ for stabilized LDPE.

CONCLUSION

The temperatures of the tests on different polyethylene are well above the glass transition temperature of such material. At this temperature polyethylene is semi crystalline and has a low amorphous character.

This feature (high degree of crystallinity) gives a polyethylene very important barrier effects for virtually all molecules. This explains the fact that the permeant quantities measured are very low.

Neutral LDPE has a diffusion coefficient greater than stabilized LDPE. This means that sorption is faster in the former than the latter. Permeation measurements performed allowed us to compare the qualities of polyethylene film manufactured in Algeria compared with data from the literature and determine the differences that exist between neutral and stabilized polyethylene. The permeation coefficients are measured when the system is fully established; the variations of this property are less pronounced than those of diffusion. However, the neutral LDPE (P = 32 Barrer) appears to be less permeable than stabilized LDPE (P = 43 Barrer). The results show that Algerian polyethylene has barrier properties, particularly for water, much higher compared to literature data. Stabilized polyethylene is more permeable than neutral material. However, the establishment of steady flow in polyethylene is slower than in the neutral polyethylene. This difference may be due to the stabilizer, the Hindered Amine Light Stabilizer (HALS) molecules occupy a number of sites on the surface of the material.

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